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Microstructural Characterization of Excel Zirconium Alloy

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Abstract

Excel zirconium alloy (Zr-3.5Sn-0.8Mo-0.8Nb) was manufactured in the 80's within the research programs for the development of high strength materials for CANDU (CANada Deuterium Uranium) pressure tubes. Excel test results showed a better dimensional stability, a higher creep resistance and its hydrides are less susceptible to reorientation during service, compared with the current material in use, Zr-2.5Nb. These factors extend the useful life of the tubes and make Excel a good option for the production of pressure tubes. The aim of the present work is to characterize the microstructure of this alloy analyzing specimens with different contents of hydrogen. The phases were studied using optical microscopy, SEM, TEM and X-ray diffraction. The quantitative chemical analysis was performed using EDS technique.

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*Keywords:*Zirconium alloys; Excel alloy; pressure tube; microstructure; hydrides.

1. Introduction

Zirconium alloys are used in nuclear applications due to the combination of good mechanical properties such as high strength and creep resistance, reasonable resistance to corrosion and low neutron capture cross-section.

The design of Generation IV CANDU reactors requires higher creep resistant alloys than Zr-2.5%Nb which is currently used for the production of pressure tubes. For this purpose Excel alloy (Zr-3.5%Sn-0.8%Mo-0.8%Nb) was developed in the 80's by AECL Chalk River Nuclear Laboratories and the tests performed showed a higher tensile

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strength, a lower creep deformation and a higher dimensional stability during operation (Cheadle et al., 1980; Ibrahim et al., 1985).

A very important parameter in the safety of the pressure tubes is the presence of zirconium hydrides. These brittle platelets can affect the tube tolerance to longitudinal defects during a reactor shut down. Under certain conditions of stress, temperature and hydrogen concentration, the component is susceptible to failure through the mechanism of delayed hydride cracking (DHC). Excel alloy exhibits higher resistance to hydride reorientation under stress, which make more difficult crack initiation and the subsequent propagation through DHC (Ells et al., 1995).These comparative advantages make Excel a good candidate to replace Zr-2.5Nb alloy. Therefore, it is important to study and characterize the microstructure of this particular zirconium alloy, which allows the prediction of the material performance in nuclear applications.

In the present work the microstructure of Excel samples has been studied by optical, scanning (SEM) and transmission electron microscopy (TEM) techniques. The phase identification and the textural effects in the samples were performed using X-ray diffraction (XRD). The chemical composition was measured by energy dispersive X-ray spectroscopy (EDS).

2. Experimental method

The material used in this work came from an Excel pressure tube manufactured by AECL (Cheadle et al., 1984). The chemical composition is shown in Table 1.

Table 1. Chemical composition of the studied Excel pressure tube.

Tube N°	Sn (*wt%*)	Mo (*wt%*)	Nb (*wt%*)	O (*ppm*)	H (*ppm*)	Zr
254 Front	3.38	0.78	0.82	1118	54	Balance
254 Back	3.47	0.81	0.80	1115	38	Balance

Excel pressure tube was fabricated according to CANDU specifications (Cheadle et al., 1980), by hot extrusion at a ratio of 13.5:1 after preheating to 760°C, followed by 5% cold drawing. The last stage consisted of a stress relief treatment at 400°C for 24 hours.

The samples analyzed in this study were taken from specimens with different hydrogen concentrations, provided by Hydrogen in Materials Division of CNEA. Specimens were cut into radial-circumferential (RC) and radial-axial (RA) sections and the obtained samples were initially studied by optical and scanning electron microscopy (SEM) techniques. For this purpose, the samples were ground with SiC papers followed by chemical polishing using a solution of 48% lactic acid, 48% HNO_3 and 4% HF, to reveal the hydrides and the present phases in the material.

The SEM micrographs were taken using a FEI Quanta 200 microscope operating in the secondary electron mode at 25 kV and a working distance between 8 and 14 mm. The image analysis was done using the Scandium SEM software and the hydrides size was measured and recorded.

X-ray diffraction (XRD) tests were performed in a Philips PW 3710 diffractometer operating at 40 kV with copper anode without monochromator. The step size used was 0.026 and the time per step was 250 seconds. The massive samples selected for XRD were taken from the as-received pressure tube material (0ppm of hydrogen charge) and from specimens with 64 and 122ppm of hydrogen.

The samples for transmission electron microscopy (TEM) were cut into thin slices followed by hand grinding on P600 SiC paper to a thickness of 0,15mm. After that, the foils were punch into 3 mm disks which were then thinned electro-chemically using a solution of 90% ethanol and 10% perchloric acid at -45ºC in a Tenupol-5 twin-jet electropolisher.

Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis were carried out in a Philips CM 200 equipped with an EDAX detector. The operating conditions for EDS study were an accelerating voltage of 160 kV and a beam size between 25 to 35 nm for all the samples. The quantitative chemical analysis was done using the TEM Genesis software. The KAB factor was selected according to the Mott Massey theoretical model applying a Gaussian fit.

3. Results and Discussion

3.1. Optical and Scanning Electron Microscopy

Excel alloy exhibit a duplex microstructure consisted of elongated hexagonal α-grains and a thin grain boundary network of cubic β-phase. The thickness of α-grains in the radial direction is 0.62μm and the dislocation density is 8.4 x 10^{14} m^{-2} (Cheadle et al.,1980).The microstructure of the as-received material on the RC plane is shown in Fig. 1. The bright area corresponds to β-phase and some hydrides platelets can be seen as dark fringes.

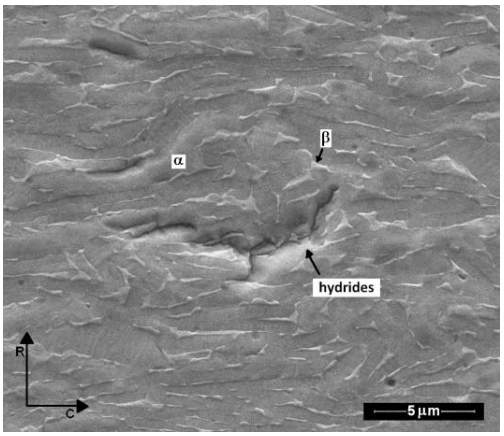

Fig. 1. SEM micrograph showing Excel alloy microstructure at 12000 X.

Optical microscopy technique allowed the easy identification of the hydride phases with different sizes and orientations. Fig.2 shows optical micrographs of two sets of samples. Fig.2(a) and (b) correspond to RC and RA planes of samples that were taken from the as-received pressure tube (0ppm), while Fig.2(c) and (d) show the same planes for a sample with 62ppm of hydrogen.

The hydrides are clearly observed in contrast and have a platelet-like morphology forming in some areas clusters of many hydrides platelets. The hydrides could be seen even in the as-received pressure tube material (0 ppm samples) due to the concentration of hydrogen incorporated during the fabrication which is enough to induce the formation of these phases. Perovic et al. (1983) studied the precipitation of hydrides in α/β zirconium alloys and corroborated that "macroscopic" hydride plates observed using optical microscopy, actually are stacks of smaller hydrides having habit planes close to (0001) basal plane. This observation is consistent with the information reported by Tulk et al. (2012) who suggested that alloys with a highly refined microstructure and small grain size, such as Zr-2.5Nb and Excel pressure tube material, tend to form macroscopic hydrides composed of many hydrides platelets. The proposed origin of the hydride platelets is a shear nucleation and growth of the hydride phase where the strain field caused by existing hydrides serves to nucleate smaller daughter hydrides (Perovic et al., 1983).

The hydrides at the RA planes are aligned in relation to the axial direction, Fig. 2(b) and (d), contrary to what occurs in the RC hydrides that do not follow a preferential direction, Fig 2(a) and (c). The measurements made using Scandium software have allowed to check that hydrides platelets in RA planes are larger (2 to 82μm) than those in the RC planes (1 to 53μm).

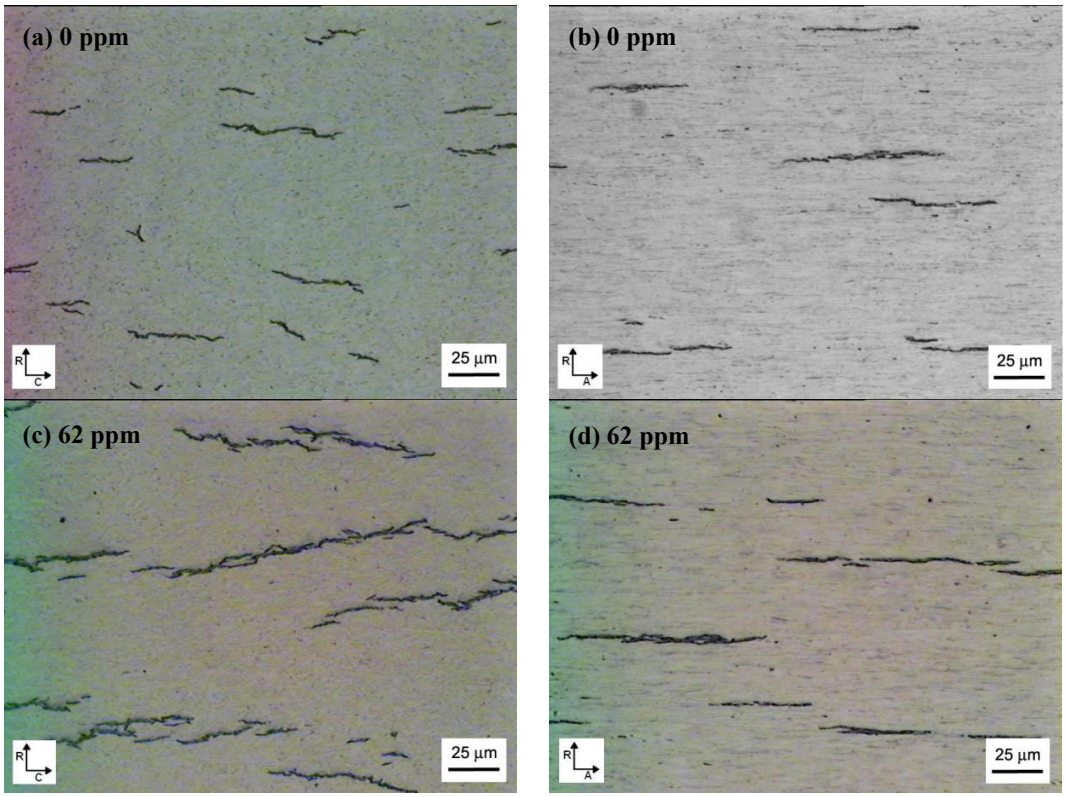

Fig. 2.Optical micrographs showing Excel samples with 0 ppm of hydrogen, (a) and (b); and 62 ppm, (c) and (d).

3.2. X-Ray Diffraction

The identification of the present phases in the radial-circumferential (RC) and radial-axial (RA) planes of three chosen samples was performed by X-Ray diffraction (XRD). The XRD patterns obtained for 0 ppm, 64 ppm and 122 ppm of hydrogen are presented in Fig.3.

Peaks associated with hexagonal close-packed (hcp) α-Zr phase, body-centered cubic (bcc) β-Zr phase and face-centered cubic (fcc) δ-hydride were identified.

There is a slight displacement of the (110) β-Zr peak with respect to the theoretical peak, which is probably related to the presence of Nb and Mo, β-stabilizers elements that are concentrated in this phase and produce changes in the crystal lattice.

The δ-zirconium hydrides were identified by the (111) peaks that are only present in the RA samples with 64 and 122 ppm of hydrogen. It is expected to find δ-$ZrH_{1.6\text{-}1.7}$ hydrides because they were reported by Tulk et al. (2012) as the stable phase below the hydrogen terminal solid solubility of dissolution. Furthermore, δ-$ZrH_{1.6\text{-}1.7}$ phase is favored by slow cooling rates, such as those the material is subjected after the final heat treatment at 400ºC during the last stage of manufacture.

The (0002) and (10$\bar{1}$0) α-Zr high intensity peaks at the RA and RC planes respectively, indicate that Excel tube samples have strong crystallographic texture produced during extrusion and cold working fabrication steps. The preferential orientation of the α-grains was confirmed with the data reported by Cheadle et al. (1980), who made measurements of crystallographic texture in Excel tubes using X-ray diffraction and determined that most of the α-grains are oriented with their basal planes normal near to the transverse direction. This could be appreciated from the resolve fraction of basal poles in the transverse direction that was 0.65 while in the radial and longitudinal directions were 0.26 and 0.09 respectively.

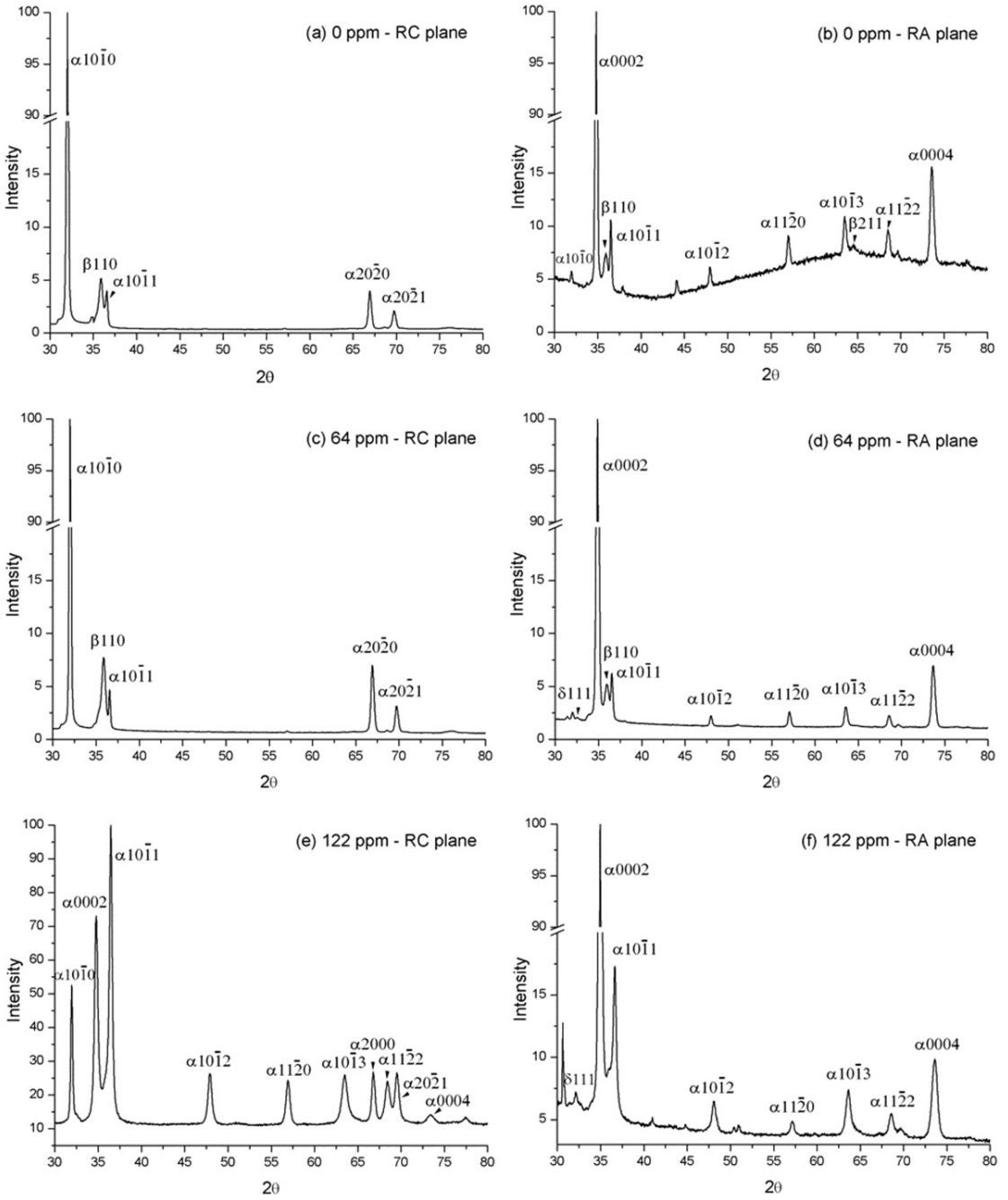

Fig.3. XRD patterns from as-received material (a) and (b), with 64 ppm (c) and (d), and 122 ppm of hydrogen (e) and (f).

The XRD patterns of RA planes in the samples with hydrogen concentration of 64 and 122 ppm allowed to confirm the orientation ratio {0002}Zr(α) // {111}ZrH(δ) between the matrix and the δ-zirconium hydride, which has been verified by SEM, TEM and synchrotron diffraction techniques in previous researches (Perovic et al., 1983; Une et al., 2004).

3.3. TEM and EDS analysis

The samples selected for transmission electron microscopy (TEM) were taken from the as-received pressure tube material. The extrusion at 850°C in the two phases (α+β) region as well as the subsequent cold working step, produce an elongated grain structure and textural effects. The elongated α-Zr grains are surrounded by a thin network of retained β-Zr, as can be seen in Fig. 4. It is known that Sn is an α-stabilizer that has a solid solution strengthening effect. On the other hand, Nb and Mo are β-stabilizers elements that produce a more resistant two-phase microstructure. This dual phase structure restricts the grain growth and leads to a finer grain size in Excel compared to other single-phase zirconium alloys. Cheadle et al. (1980) reported grains sizes in the radial direction between 0.58 and 0.74 μm for annealed and cold worked Excel samples.

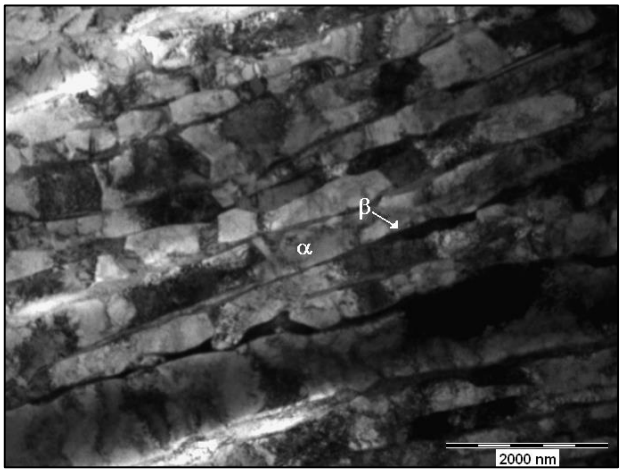

Fig. 4. TEM micrograph showing the microstructure of as-received Excel pressure tube

Fig. 5 shows the microstructure of Excel material at higher magnification. The α-Zr phase is formed by elongated grains wider than β-Zr grains. In Fig. 6(a) is shown a central α-Zr grain that satisfies the Bragg conditions and its corresponding selected area diffraction (SAD) pattern. Fig. 6(b) shows a particular β-Zr grain formed at the corners of α-Zr grains with its corresponding SAD pattern.

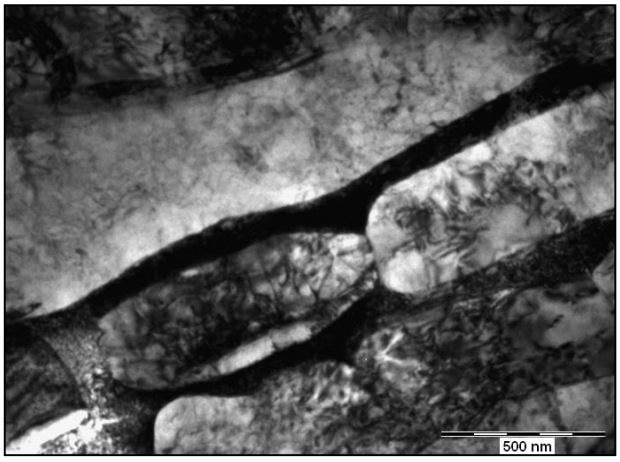

Fig. 5. Excel sample showing α-Zr grains and β-Zr filaments.

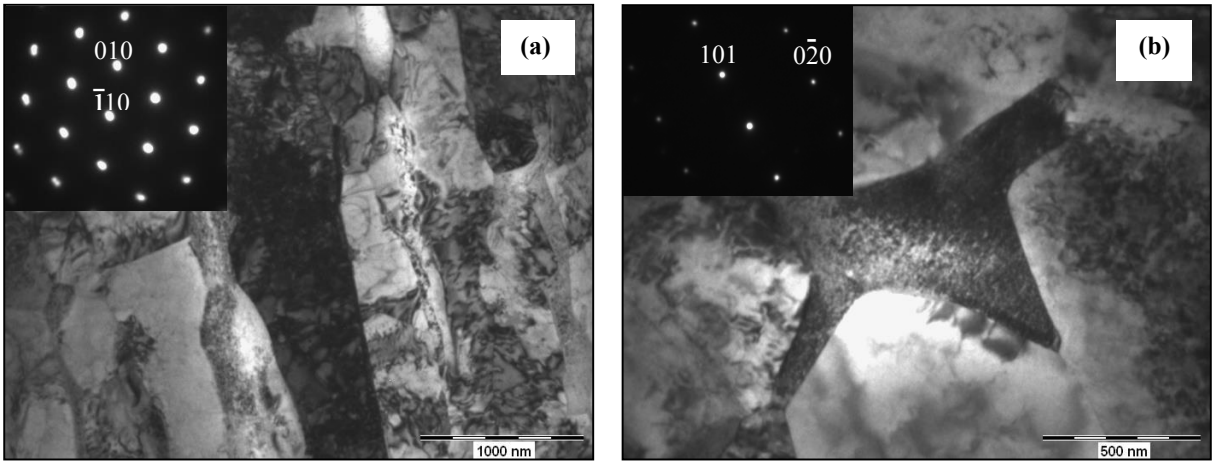

Fig. 6. TEM micrographs showing (a) α-Zr grain in Bragg condition, axis zone Z = [0001], (b) irregular shape β-Zr grain Z = [$\bar{1}$01].

The EDS analysis has revealed that the α-phase is rich in Sn, while Nb and Mo are concentrated in β-phase.

The Table 2 summarizes the results of quantitative EDS analysis on α-Zr and β-Zr phases. At least 50 spectrums obtained from as-received pressure tube material were selected for the analysis. The error in the measurements corresponds to the standard deviation.

Table 2. Chemical composition (%wt) of α-Zr and β-Zr phases.

Element	α-grains	β-grains
Zr	95.99 ± 0,41	87.57 ± 1.18
Sn	4,01 ± 0,41	1.92 ± 0.55
Nb	-	3.83 ± 0.58
Mo	-	6.68 ± 0.71

TEM observations have allowed to detect ω-phase that is produced by partial decomposition of metastable β-Zr phase. This transformation has been reported by several authors in Zr-2.5Nb alloys (Aldridge et al., 1972; Griffiths et al., 2008).When body-centered-cubic β-Zr filaments are annealed at temperatures below 600°C, as in the final stress-relief treatment at 400°C, decompose into hexagonal-close-packed ω-phase particles that are depleted in β-stabilizers elements (Nb and Mo). This results in an enrichment of remaining β-phase in Nb and Mo. The characteristic cuboidal morphology of ω-phase formed inside β-Zr grain is shown in the Fig. 7(a) and (b) as bright-field and dark-field images respectively. Fig. 7(c) present ω-particles formed inside a β-Zr grain and the respective SAD pattern showing reflections from bcc β-phase and hcp ω-phase (red circles).

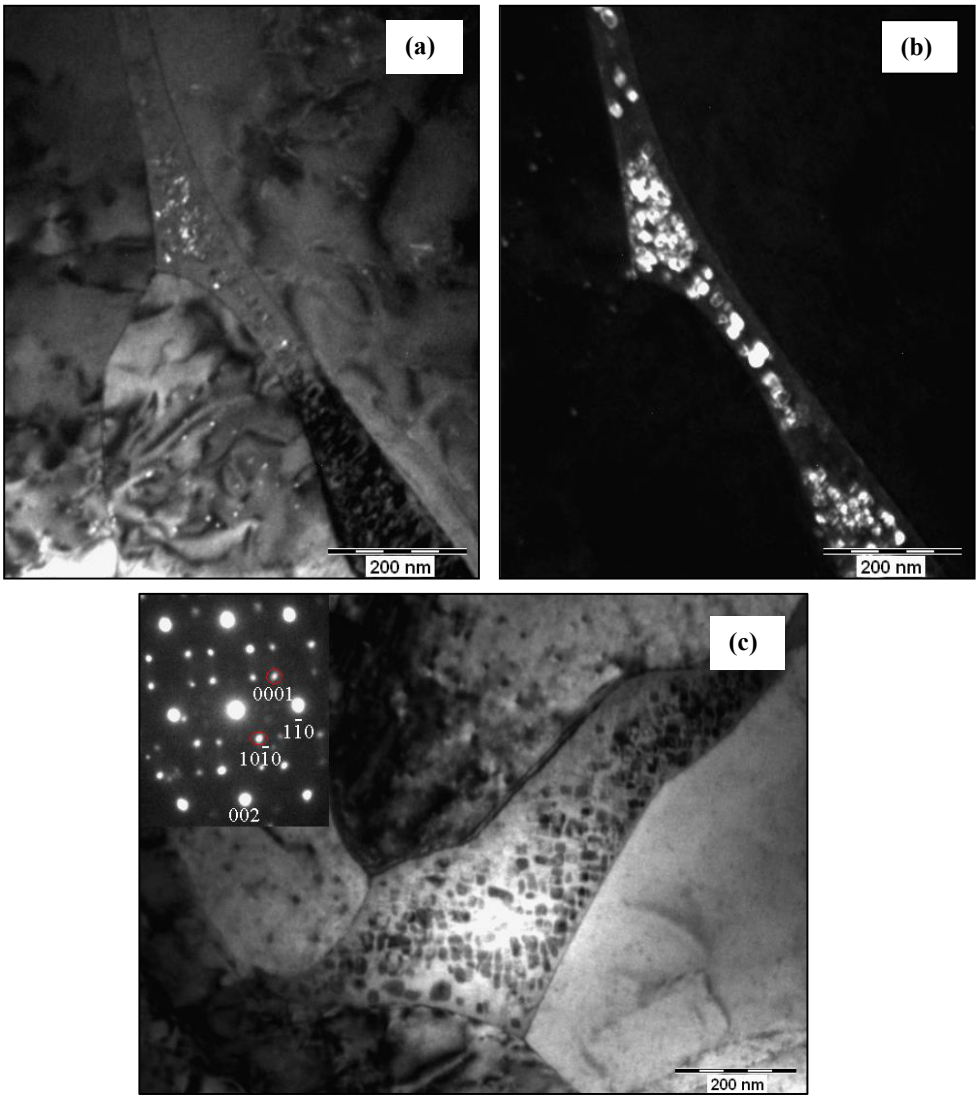

Fig. 7. TEM micrographs showing ω-particles formed inside β-Zr grains, (a) bright-field image, (b) dark-field image, (c) bright-field image and SAD pattern Z(β) = [110] and Z(ω) = [$1\bar{2}10$].

4. Conclusions

The pressure tube samples of Excel that were examined in this work have exhibited a duplex microstructure consisting of elongated α-Zr (hcp) grains surrounded by thin filaments of β-Zr (bcc) phase. This is according to the treatment received by the material during its manufacture. The stages of extrusion and cold working produce textural effects in the grains which are shown in the diffractograms as intense peaks of specific families of planes. The ($10\bar{1}0$) and (0002) poles of α-Zr grains predominate in the RC and RA planes, respectively.

The presence of hydrogen promotes the δ-hydrides precipitation even in the samples without hydrogen charge (0 ppm) due to the initial hydrogen concentration in the starting material. The size of the observed hydrides corresponds to the order of few microns. These hydrides are aligned in relation to the tube axial direction with an orientation relationship {0002}Zr(α) // {111}ZrH(δ) between α-grains and δ-hydrides.

The TEM observations and EDS technique have showed that Sn is concentrate in α-grains while Nb and Mo are present in the β-grains. β-Zr phase is metastable and decomposes during the stress-relief treatment at 400°C, forming ω-particles that are depleted in β-stabilizing elements surrounded by a matrix rich in these elements.

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